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(54) Process and apparatus for determining foreign substances in granular media.

(57) The invention relates to a process and apparatus for determining foreign substances in granular media by measuring the spectral absorption in the infrared range or the spectral fluorescence. The invention serves to quantitatively and quantitatively determine foreign substances in granular media without taking and extracting samples as well as to quantitatively determine matrix influences of the soil structure and soil moisture.
By measuring the spectral distribution of the light reflected by the granular medium, the simultaneous graphic measuring of the structure of the granular medium, the determining of the average grain size as well as of the effective water stratum thickness of the granular medium, the concentration of water as well as the concentration of foreign substances in the granular medium is calculated. The combination of illumination, camera for the graphic recording of the soil structure and recording of the infrared radiation by way of an optical fibre in a measuring head permits the determination of the foreign substances directly in the granular medium.

Description

The invention relates to a process and apparatus for determining foreign substances in granular media by measuring the spectral absorption in the infrared range or the spectral fluorescence.

An extremely important environmental problem nowadays is the contamination of soil. To evaluate this, drill cores are taken from the soil. The foreign substances, generally harmful substances, are extracted from the soil with solvents and then analysed by standardised spectroscopic or chromatographic methods. This process is time-consuming and requires a great amount of equipment. The solvent pollutes the environment.

A direct determination of the harmful substances in the soil was as yet not possible seeing that uncontrolled matrix influences were superimposed on the test results. Dominating disturbing influences are the soil structure and soil moisture.

It is, therefore, the object of the invention to qualitatively and quantitatively determine foreign substances in a granular medium without taking or extracting samples, as well as to quantitatively determine the matrix influences soil structure and soil moisture.

According to the invention this object is achieved by the characterising features of patent claims 1 to 4 and 10.

Advantageous embodiments form the subject of the dependent claims, the content of which claims herewith expressly becomes an integral part of the present description, without having to repeat the wording here.

The invention will be explained with reference to an exemplified embodiment based on drawings, wherein:

Fig. 1 illustrates the process based on a flow sheet for determining foreign substances in the soil,

Fig. 2 shows the unfolding of the spectrum with the spectral inherent function of the measuring system and the absorption spectrum of the soil moisture.

Fig. 3 shows the measuring head for determining foreign substances in the soil.

Fig. 4 is a diagrammatic representation of the measuring device for determining foreign substances in the soil.

The determination of the foreign substances takes place according to Fig. 1 by two separate measuring cycles. Light with visible and infrared portions is directed onto the soil that contains the foreign substances. During the first measuring cycle the infrared light, after reflection on the soil

contaminated by foreign substances, is recorded by a spectrograph. The measured reflection spectrum $S_{total(\lambda)}$ is stored in a computer. As next step the spectrum $S_{total}(\lambda)$ is standardised with the spectral inherent function of the measuring system $S_{inherent}(\lambda)$ according to the equation $S_{residual}(\lambda) = S_{total}(\lambda) / S_{inherent}(\lambda)$. $S_{residual}(\lambda)$ contains the absorption bands of the foreign substances as well as of the water that is always present. Because of its broadband absorption, water disturbs the quantitative analysis of foreign substances. Consequently, the absorption of the water must be determined and must be taken into account in the quantitative analysis. By two measures valued at the spectral points λ_3 and λ_4, which lie outside the band range of the foreign substances, the effectively penetrated water stratum thickness X_{water} is determined. Based on the known pattern of the absorption coefficient of water $\alpha_{water}(\lambda)$, the transmission spectrum of the acting water stratum can be calculated according to the equation $S_{water} = e^{-\alpha_{water}(\lambda)*X_{water}}$. The spectrum $S_{residual}(\lambda)$ is thereupon obtained with $S_{water}(\lambda)$ according to the equation $S_{foreign}(\lambda) = S_{residual}(\lambda)/S_{water}(\lambda)$.

What remains are the absorption bands of the foreign substances from which the modulation MOD of the spectrum is calculated according to the equation MOD = $(I_1 - I_2)/I_1$. I_1 is the intensity of the reflected IR-radiation outside the absorption bands of the foreign substances at the wavelength λ_1 and I_2 is the corresponding intensity in the maximum of the absorption bands at the wavelength λ_2. Based on the known absorption coefficient $\alpha_{foreign}$ for the wavelengths λ_1 and λ_2, the effective thickness of the foreign substance stratum $X_{foreign}$ can be determined.

In the second measuring cycle the radiated visible light is used for a graphic recording of the soil structure. By means of a camera lens the soil surface is depicted on a photo detector cell, which records a one-dimensional picture. The one-dimensional graphic information is processed in a computer. By averaging all detected grain sizes, an average grain size d_{grain} is determined by the computer.

A spectrum developed according to Fig. 1 is illustrated in Fig. 2. The foreign substance in question here is mineral oil hydrocarbon (MHC). The spectrum $S_{total(\lambda)}$ was recorded on soil contaminated by MHC. After standardisation with the spectral inherent function of the measuring system, the spectrum $S_{residual}(\lambda)$ is obtained which includes the absorption band of water and MHC. In a further calculation operation the spectrum $S_{residual}(\lambda)$ is developed with the spectrum of the water $S_{water}(\lambda)$. What remains are the absorption bands of the MHC, from which the modulation MOD = $((I_1 - I_2)/I_1$ for the MHC contamination is calculated. The water stratum thickness X_{water} effective for the measured absorption is calculated according to the equation :

$X_{water} = \ln[S_{residual}(\lambda_3) / S_{residual}(\lambda_4)] / [\alpha_{water}(\lambda_4) - \alpha_{water}(\lambda_3)]$. $\alpha_{water}(\lambda)$ is the absorption coefficient of water and is known. λ_3 and λ_4 are two wavelengths at which the MHC has no absorption bands.

With the water stratum thickness X_{water} and the average grain size d_{grain}, the water concentration in the soil is calculated as $C_{water} = P(d_{grain}) * X_{water}$.

$P(d_{grain})$ is a polynomial of the 5th degree, the coefficients of which are calculated according to a calibration measurement.

Similar to the water, the effective MHC-layer thickness $X_{foreign}$ is calculated according to the equation $X_{foreign} = \ln(1\text{-MOD})/[\alpha_{foreign}(\lambda_1) - \alpha_{foreign}(\lambda_2)]$.

$\alpha_{foreign}(\lambda_2)$ is the absorption coefficient of MHC in the maximum of the bands. It is determined with absorption measuring devices or taken from standard literature and made available to the computer in a databank for the analytical evaluation. $\alpha_{foreign}(\lambda_1)$ is in a first approximation taken as equal to zero. With the effective MHC layer thickness $X_{foreign}$ and the average grain size d_{grain} the HMC-concentration is calculated as $C_{foreign} = P(d_{grain}) * X_{foreign}$.

$P(d_{grain})$ is a polynomial of the 5th degree, the coefficients of which are calculated according to a calibration measurement.

The measuring of the MHC-containing soil is repeated for a multitude of individual measurements over a large soil surface and the test results are averaged over the number of measurements. In the case of an inhomogeneous distribution of the MHC in the soil, the average MHC-concentration can in this way be determined without the MHC having to be extracted from the soil with solvents.

A measuring head for determining the foreign substances in the soil is illustrated diagrammatically in Fig. 3. An incandescent lamp (3) with tungsten filament directs light with visible and infrared spectrum portions through a sapphire window (7) onto the soil (2). Via a camera lens (6), the photo detector cell (5) records a one-dimensional picture of the soil structure and transmits this via the cable (8) to an evaluation and control unit. The infrared light portion reflected by the soil is recorded by the end of a optical fibre (4) and fed to the spectrograph of the evaluation and control unit. All elements of the measuring head are mounted in a cylindrical housing (1) with a cone-shaped part at one end. The housing is made of steel.

The complete apparatus for measuring foreign substances in granular media consists according to Fig. 4 of the measuring head (11), the connection cable (9) and the evaluation and control unit (10). The connection cable (9) connects the optical fibre (4) and the electricity supply cable for the lamps and the photo detector cell (8) in a housing. The evaluation and control unit comprises the spectrograph for recording the IR-spectrums as well as a PC. In addition to controlling the system and the evaluation of the spectrums, this also ensures the dialogue with the user of the system. The apparatus according to Fig. 4 permits measuring the foreign substances directly in the granular medium. A sample extraction is not required.

To measure the spectral fluorescence of the harmful substances in granular media, an additional optical fibre is introduced into the measuring head (11). Through same laser pulses of a N_2 laser

with the wavelength 337 nm are directed onto the soil. The fluorescence light of the sample is fed via the optical fibre (4) to a spectrograph. For quantitative evaluations of fluorescent foreign substances the grain size is taken into account in the manner as described for the infrared spectroscopy.

List of reference numerals:

1 Measuring head housing
2 Granular medium
3 Light source
4 Optical fibre
5 Photo detector array
6 Camera lens
7 Sapphire disk
8 Electrical connection
9 Connection cable
10 Evaluation and control unit
11 Measuring head.

Patent claims

1. Process and apparatus for determining foreign substances in granular media by measuring the spectral absorption in the infrared range or the spectral fluorescence, **characterised in that** from a measuring probe light is directed onto the granular medium and the light reflected back by the granular medium is recorded for a spectroscopic measuring, the structure of the medium is recorded by the measuring probe as graphic information and furthermore the average grain size of the medium is deduced from the graphic information by graphics-processing operations.

2. Process according to claim 1, characterised in that during the spectral absorption measuring the spectrum reflected back by the granular medium, at several scanning values outside the absorption bands of the foreign substances the absorption bands of water are measured and by mathematical operations the effective water stratum thickness is ascertained and from this the water concentration is determined.

3. Process according to claim 1 and 2, characterised in that the measured spectrum of the granular medium is developed with the absorption bands of the water and the spectral inherent function of the measuring system, and from the corrected spectrum and the average grain size of the medium the foreign substance concentration is determined.

4. Process according to at least one of the claims 1 to 3, characterised in that the measuring is repeated for a multitude of individual measurements over a larger soil surface and the measured results are averaged over the number of measurements.

5. Process according to at least one of the claims 1 to 4, characterised in that the measured reflection spectrum $S_{total}(\lambda)$ is standardised with the spectral inherent function of the measuring system $S_{inherent}(\lambda)$ according to the equation

$$S_{residual}(\lambda) = \frac{S_{total}(\lambda)}{S_{inherent}(\lambda)}$$

6. Process according to at least one of the claims 1 to 5, characterised in that the effective water stratum thickness is calculated according to the equation

$$X_{water} = \frac{1}{\alpha_{water}(\lambda_4) - \alpha_{water}(\lambda_3)} * \ln\left[\frac{S_{residual}(\lambda_3)}{S_{residual}(\lambda_4)}\right]$$

and the water concentration in the granular medium is determined according to the equation $C_{water} = P(d_{grain}) * X_{water}$.
wherein $P(d_{grain})$ is a polynomial of the 5th degree, the coefficients of which are calculated according to a calibration measurement.

7. Process according to at least one of the claims 1 to 6, characterised in that the spectrum of the foreign substances is developed with the absorption bands of the water according to the equation

$$S_{foreign}(\lambda) = \frac{S_{residual}(\lambda)}{S_{water}(\lambda)}$$

8. Process according to at least one of the claims 1 to 7, characterised in that the spectrum of the foreign substances layer thickness is calculated according to the equation

$$X_{foreign} = \frac{\ln(1 - MOD)}{[\alpha_{foreign}(\lambda_1) - \alpha_{foreign}(\lambda_2)]}$$

and the foreign substance concentration according to the equation

$$C_{foreign} = P(d_{grain}) * X_{foreign}.$$

wherein $P(d_{grain})$ is a polynomial of the 5th degree, the coefficients of which are calculated according to a calibration measurement.

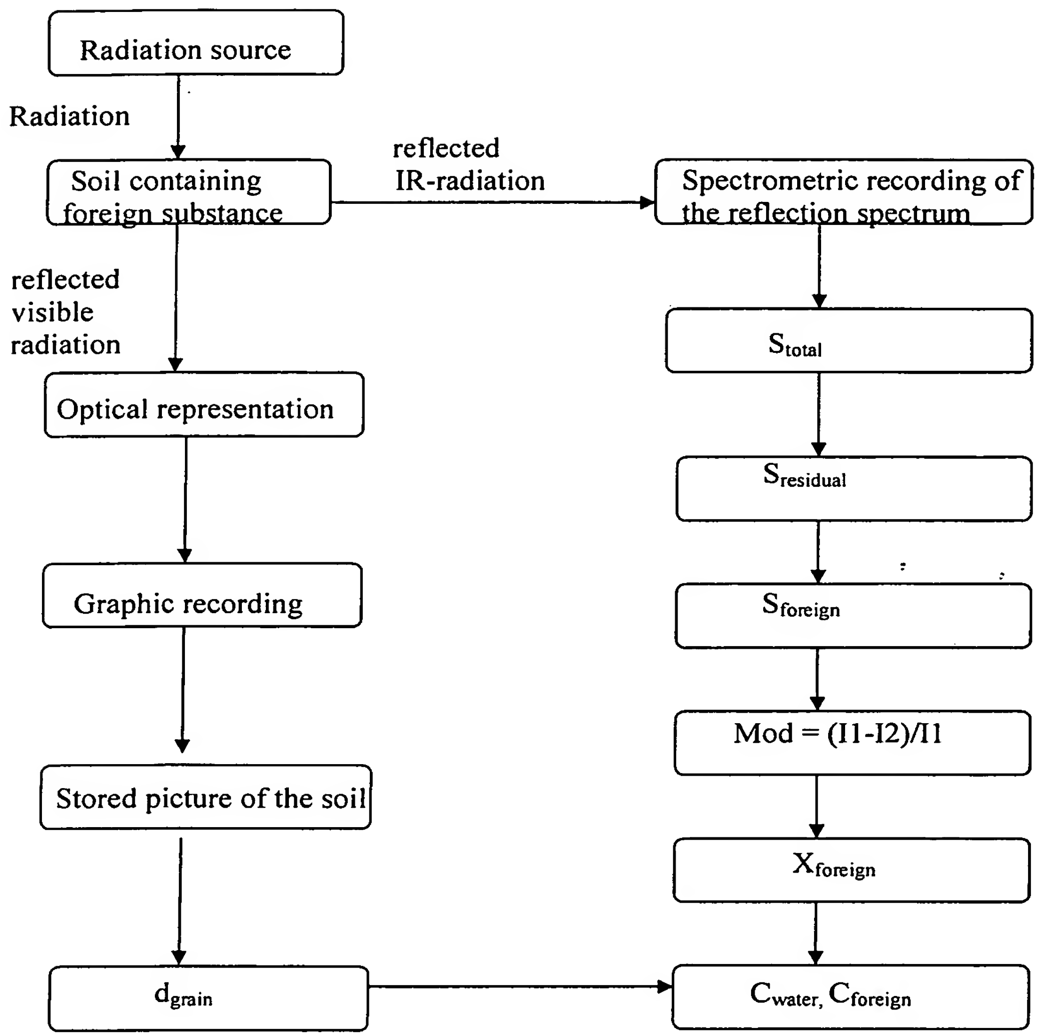
9. Process according to claim 1, characterised in that with the spectral fluorescence measurement the light reflected back by the granular medium is measured and via mathematical operations using the average grain size a conclusion is draw regarding the foreign substance concentration.

10. Apparatus for the implementation of the process according to at least one of the claims 1 to 9, characterised in that in a measuring head (11) light sources (3) with infrared and visible spectral portions are arranged in front of a window (7), in front of the window a camera lens (6) and a photo detector array (5) are arranged for recording a one-dimensional picture of the soil (2) and furthermore, in order to collect the infrared light reflected by the soil (2) the end of an optic fibre is arranged in front of the window (7).

11. Apparatus according to claim 10, characterised in that the electrical connection (8) to the light sources (3) and to the photo detector array (5) as well as the optic fibre (4) is combined in a connection cable (9) and the overall measuring apparatus consists of measuring head (11), connection cable (9) and evaluation and control unit (10).

12. Apparatus according to claim 10 and 11, characterised in that the photo detector array is a photo detector cell.

With 4 pages of drawings



Radiation source
Radiation
Soil containing foreign substance
reflected IR-radiation
Spectrometric recording of the reflection spectrum
reflected visible radiation
S_{total}
Optical representation
$S_{residual}$
Graphic recording
$S_{foreign}$
Mod = (I1-I2)/I1
Stored picture of the soil
$X_{foreign}$
d_{grain}
C_{water}, $C_{foreign}$

Fig. 1.